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PUBLISHED NONLINEAR OPTICAL USES OF ZINC GERMANIUM DIPHOSPHIDE

NILS C FERNELIUS

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13. ABSTRACT *(Maximum 200 words)*

This report gives capsule summaries of all published work using the nonlinear optical properties of zinc germanium diphosphide (ZnGeP2). It is organized in several groupings-early American work, Russian, and recent Western work. A general bibliography is given as an appendix.

14. SUBJECT TERMS
zinc germanium diphosphide, ZnGeP2, ZGP, second harmonic generation (SHG) optical parametric oscillator (OPO), sum frequency generation (SFG), difference frequency generation (DFG)

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PUBLISHED NONLINEAR OPTICAL USES OF ZINC GERMANIUM DIPHOSPHIDE

by Nils C. Fernelius

INTRODUCTION

Currently the crystal of choice for optical parametric oscillators (OPO) operating in the 3-5 µm atmospheric window range is zinc germanium diphosphide (ZGP). The OPO is usually pumped by a holmium laser operating around 2 µm. Several factors delayed the common usage of ZGP in nonlinear optical (NLO) devices. First there was the problem of obtaining crack free crystals. The other serious problem, still not completely resolved, is a native defect optical absorption shoulder on the short wavelength side of the transparency window which extends beyond 2 µm. This degrades high power operation when using a 2 µm pump.

The first NLO uses of ZGP were demonstrated at Bell Labs in 1971 as a result of the interaction of the NLO group with the ternary semiconductor group. Most of the work entailed sum and difference frequency generation (SFG) & (DFG) plus one second harmonic generation (SHG) paper. There were five papers by G.D. Boyd et al. in 1971-1972. The work was summarized in an Avionics Lab tech report by Nichols, Corbin and Donlan in 1974. Due to reorganizations, both civilian and military, work in the area ceased. For almost the next 20 years, all research on this material was done in the Soviet Union. In the last few years, NLO ZGP work in the West has been revived.

This work will try to summarize the literature in three categories: early American, Russian, and recent Western work. Each category consists of a list of papers, the affiliation of the authors and a capsule summary of the work. The following were grouped in the Russian section: the paper by Churnside et al. since it was performed on a crystal brought from Russia when Gribenyukov was on sabattical, some later work of Gopal Bhar even though it was performed in India, and the work of Vodopyanov after he started working at Imperial College, London.

Gopal Bhar did some significant work which does not fit in the above categories. Initially he published a number a papers obtaining Sellmeier equations by reanalyzing Boyd's data. From this he published a number of SHG and OPO tuning curves including temperature dependences. These papers will be listed in the general bibliography combining all categories.

EARLY AMERICAN WORK

A1 - G.D. Boyd, E. Buehler & F.G. Storz, Bell Telephone Laboratories, Murray Hill, New Jersey

Linear and nonlinear optical properties of $ZnGeP_2$ and CdSe
Appl. Phys. Lett. **18** 301-304 (1971)

measures n_o, n_e, dn_o/dT, dn_e/dT

shows three-frequency phase matching plots for $\theta_m = 90^o, 74^o, 66^o, 60^o$

A2 - G.D. Boyd, W.B. Gandrud & E. Buehler, BTL
Phase-matched up conversion of 10.6-μ radiation in $ZnGeP_2$
Appl. Phys. Lett. **18** 446-448 (1971)

Sum frequency generation (SFG): 10.6 & 1.06 μm

Experimental: $\theta_m = 84^o$, $d\theta_m/dT = -0.007$ deg/^{o}C

crystal length = 1 cm

A3 - G.D. Boyd, T.J. Bridges, C.K.N. Patel & E. Buehler, BTL
Phase-matched submillimeter wave generation by difference-frequency mixing in $ZnGeP_2$
Appl. Phys. Lett. **21** 553-555 (1972)

Difference frequency generation (DFG) using two step-tunable CO_2 lasers
Phase-matched outputs between 70 cm^{-1} (143μm) and 110 cm^{-1} (91μm)

A4 - Elgene R. Nichols, John C. Corbin,Jr. and Vincent L. Donlan
Avionics & Materials Laboratories, Wright-Patterson AFB, Ohio
A Review of Parametric Oscillators and Mixers and an Evaluation of Materials for 2-6μm Applications
Air Force Avionics Laboratory Tech Report
AFAL-TR-74-161, July, 1974

gain/watt 1cm long crystal vs output wavelength plots for pump wavelengths 1.06, 1.3, 1.83, and 2.1 μm. pp.22-24

Optical parametric oscillator (OPO) performance for λ_{pump} = 1.06, 1.3 and 2.10 μm. pp. 30-34

A5 - J.L. Shay & J.H. Wernick **Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications** , Pergamon Press, Oxford, 1975

Chapter 6 - Noninear Optical Applications pp. 153-174

RUSSIAN USE OF $ZnGeP_2$ IN NLO

R1 - N.P. Andreeva, S.A. Andreev, I.N. Matveev, S.M. Pshenichnikov & N.D. Ustinov
Parametric conversion of infrared radiation in zinc germanium diphosphide
Sov.J. Quantum Electron. **9** 208-210 (1979)
Russian reference: Kvantovaya Elektron. (Moscow) **6** 357-359 (1979)

Use as PARAMETRIC CONVERTER output @ 960 nm
PUMP CHARACTERISTICS:
Nd:YAG (1.06 μ) $\tau = 30$ ns power density = 3 MW/cm^2 rep rate = 12.5 Hz
Laser @ 3 MW/cm^2 no damage seen over 30 min
@ 20 MW/cm^2 damage after 5-10 pulses
CO_2 Laser (10.6 μ) CW power ~ 1 W
@ 10 W/cm^2 no damage over 3-4 cycles of 30 min
CRYSTAL: single crystal $ZnZGeP_2$ working faces polished
thickness 3 mm $\Theta_{pm} = 82.5^o$
α(960nm) = 10 cm^{-1}
α(1.06 μ) = 8 cm^{-1}
α(10.6 μ) = 2 cm^{-1}

R2 - Yu.M. Andreev, V.G. Voevodin, A.I. Gribenyukov, O.Ya. Zyryanov, I.I. Ippolitov, A.N. Morozov, A.V. Sosnin & G.S. Khmel'nitskii
Institute of Atmospheric Optics, Tomsk
Efficient generation of the second harmonic of tunable CO_2 laser radiation in $ZnGeP_2$
Sov. J. Quantum Electron. **14** 1021-1022 (1984)
Russian reference: Kvantovaya Elektron. (Moscow) **11,**1511-1512 (August 1984)

SHG of CO_2
PUMP CHARACTERISTICS: CW and pulsed rep rate 1.5 kHz τ = 0.1-10 ms
average power in TEM_{00} was 0.5 - 5 W depending on transition
damage threshold 60-65 MW/cm^2 @ $\lambda = 10.6$ m
no damage observed for CW of 1 kW/cm^2
best pulsed power conversion efficiency,5%, was @0.6kW pump
CRYSTAL: Bridgman mechanical & chemodynamic polishing
no AR coatings
α(2.5-12μ) less than 0.1 cm^{-1}
in 8.5-9.45 μ and $\lambda > 10.6$ m have phonon absorption
cross section area ~ 3 cm^2 $\Theta = 76^o$

R3 - Yu.M. Andreev, T.V. Vedernikova, A.A. Betin, V.G. Voevodin, A.I. Gribenyukov, O.Ya. Zyryanov, I.I. Ippolitov, V.I. Masychev, O.V. Mitropol'skii, V.P. Novikov, M.A. Novikov & A.V. Sosin Inst.Atmosph. Optics, Tomsk
Conversion of CO_2 and CO laser radiations in a $ZnGeP_2$ crystal to the 2.3-3.1 μ spectral range Sov.J. Quantum Electron. **15** 1014-1015 (1985)
Russian ref.: Kvantovaya Elektron. **12** 1535-1537 (July 1985)

4th harmonic of CO_2 efficiency ~ 0.1 % should get to 20%
2nd harmonic of CO " (0.0025-0.010)%
PUMP CHARACTERISTICS:
TEA CO_2 τ ~ 170 ns energy 200 mJ/pulse
first 2nd harmonic type I ee->o $ZnGeP_2$ in oven efficiency ~ 2%
energy 4 - 10 mJ
second 2nd harmonic crystal 5 mm $\Theta = 48°54'$ $\varphi = 0°25'$
4th harmonic at least 0.2 mJ efficiency ~ 0.1%

$\alpha(2\text{-}12\mu)$ ~ 2 cm^{-1}
CO SHG output power 8.5 W strongest line 0.8W SH 2 μW
$a(2.8\mu)$ ~2.8 cm^{-1}
$a(5\mu)$ ~3.8 cm^{-1}
CW CO @ 10 kW/cm^2 for 6 hours showed no sign of damage

R4 - K.L. Vodop'yanov, V.G. Voevodin, A.I. Gribenyukov, & L.A. Kulevskii
Institute of General Physics, Moscow
Picosecond parametric superluminescence in the $ZnGeP_2$ crystal
Bulletin of the Academy of Sciences of the USSR, Physical Series **49** 146-149 (1985)
Russian reference:
Izvestiya Akademii Nauk SSSR, Seriya Fizicheskaya **49** 569-572 (1985)

use as OPO
PUMP CHARACTERISTICS:
Erbium laser (2.94 μm) train of 25 pulses, t = 80 ps, rep rate 1 Hz,
total energy in train of 10-15 mJ

$ZnGeP_2$ CRYSTAL:
single crystal by Bridgmen
a did not exceed 0.2 cm^{-1} for $\lambda = 2.5\text{-}8.5$ μm
in three-phonon absorption band (8.3-9.5 μm) $\alpha = 0.3$ cm^{-1}(l = 8.8 μ)
calculate o-ee and o-eo tuning curves
experiment o-eo : $\Theta = 84.5°\text{-}79.3°$ covering $\lambda = 5.51\text{-}5.38$ & 6.29-6.46 μm
Crystal 42 mm long cut at an angle of 64°
max pump intensity 4×10^9 W cm^{-1}

R5 - L.I. Andreeva, K.L. Vodop'yanov, S.A. Kaidalov, Yu.M.Kalinin, M.E. Karasev, L.A. Kulevskii & A.V. Lukashev Institute of General Physics, Moscow
Picosecond erbium-doped YAG laser ($\lambda = 2.94$ μ) with active mode locking
Sov.J. Quantum Electron. **16** 326-333 (1986)
Russian Ref.: Kvantovaya Elektron. **13** 499-509 (March 1986)

use as OPO with $ZnGeP_2$

PUMP CHARACTERISTICS: $Y_3Al_5O_{12}:Er^{3+}$ $\lambda = 2.94$ µm rep rate 1-1.5 Hz
generated train with energy 12 mJ of 25 pulses with energy 0.5 mJ (+/-3%) per spike and 40+/-10 ps duration at 4th harmonic
pulse separation 6.7 ns FWHM envelope 160 ns

CRYSTAL optic axis to $\perp$ at end surface was 84°
the polar angle was $\varphi = 45°$ o-eo interaction
signal $\lambda = 6.3$ µm idler $\lambda = 5.5$ µm

R6 - V.E. Zuev, Yu.M. Andreev, V.G. Voevodin, A.I. Gribenyukov, V.A. Kapitanov, A.V. Sosnin, G.A. Stuchebrov, & G.S. Khelnitskii
Institute of Atmospheric Optics, Tomsk
Multifrequency dial sensing of the atmospheric gaseous constituents using the first and second harmonics of a tunable CO_2 laser radiation
Proceedings 13th International Laser Radar Conference, Toronto, Canada 1986, NASA Conference Publication **2413** 108-110 (1986)

SHG of CO_2
PUMP CHARACTERISTICS: 16 CO_2 wavelengths from R14 to R32
60 MW/cm² for 200 ns pulses
200 kW/cm² for CW
CRYSTAL: 10 x 20 mm cross section
3-10 mm thickness with polished ends

R7 - Yu.M. Andreev, V.G. Voevodin, A.I. Gribenyukov, & V.P. Novikov
Institute for Applied Physics, Gorki
Mixing of frequencies of CO_2 and CO lasers in $ZnGeP_2$ crystals
Sov.J. Quantum Electron. **17** 748-749 (1987)
Russian ref: Kvantovaia Elektronika **14** 1177-1178 (June,1987)

Summed CO and CO_2
PUMPS: CO_2 5.7 W CO 4.7 W
CRYSTALS:

Length mm	Θ_{pm} for normal incidence °	Azimuthal angle °	Absorption coefficient @ CO_2 in cm^{-1}	CO	CO_2+CO	Damage threshold CO_2 kW/cm²	CO
3.1	48	0	0.83	0.32	0.41	200	250
8.0	90	45	0.46	0.1	0.2		

damage threhold for pulsed CO_2 60 MW/cm² for 200 ns pulses

R8 - Yu.M. Andreev, A.D. Belykh, V.G. Voevodin, P.P. Geiko, A.I. Gribenyukov, V.A. Gurashvili & S.V. Izyumov Inst.Atmospheric Optics, Tomsk
Doubling of the emission of CO lasers with an efficiency of 3 %.
Sov.J. Quantum Electron. **17** 490-491 (1987)
Russian ref.: Kvantovaya Elektron. **14** 782-783 (April1987)
SHG of CO
PUMP: CO Q-switched energy per pulse 2 mJ @ 10 Hz; 0.6 mJ @ 100 Hz
0.1 mJ @ 200 Hz

CRYSTAL 7 mm long $\Theta = 47°30'$ $\varphi = 0$ chemodynamic polish, no AR
maximum external efficiency of whole SHG system 3.2%

R9 - Yu.M. Andreev, A.I. Gribenyukov, V.V. Zuev, N.V. Karlov, V.D. Karyshev, A.V. Kisletsov, I.O. Kovalev, A.V. Korablev, G.P. Kuz'min, L.A. Kulevskii & A.A. Nesterenko
Institute of General Physics, Moscow
Second-harmonic generation in $ZnGeP_2$ pumped by a continuously tunable CO_2 laser
Sov. Tech. Phys. Lett. **13** 595-596 (1987).
Russian ref.: Pis'ma v Zhurnal Tekhnicheskoi Fiziki **13** 1423-1426 (12 Dec 1987)

SHG of CO_2
PUMP CHARACTERISTICS:
could tune CO_2 over 9.19-9.7μm & 10.15-10.8 μm
linearly polarized 15-70 mJ, pulse length FWHM ~ 50 ns
achieved doubled tuning over 5.15-5.11, 4.80-4.73, 4.65-4.61 μm
CRYSTAL:
4.4 mm thick $\theta = 76°$ $\varphi = 0°$ $\alpha = 2.1\ cm^{-1}$
spot 1.5 mm diameter, surface damage above 65 mJ or ~ 4 J/cm^2

R10 - K.L. Vodop'yanov, V.G. Voevodin, A.I. Gribenyukov & L.A. Kulevskii
High-efficiency picosecond parametric superradiance emitted by a $ZnGeP_2$ crystal in the 5-6.3 μ range Inst. of General Physics, Moscow
Sov.J. Quantum Electron. **17** 1159-1161 (1987)
Russian ref: Kvantovaia Elektronika **14** 1815-1819 (Sept. 1987)

OPO
PUMP CHARACTERISTICS:
Er^{3+}:Cr^{3+}:YSGG yttrium scandium gallium garnet $\lambda = 2.79$ μm
$\tau = 150$ ps +/- 25 rep rate 1 Hz up to 2 mJ/spike
laser spot ~ 0.1 mm diameter (area = 0.00017 cm^2)
CRYSTAL:
Bridgman α in range 2.8-8.3 μ did not exceed 0.1 cm^{-1}
no AR coatings Type II o->eo $\theta = 84°$ $\lambda_1 = 5.96$ μm, $\lambda_2 = 5.25$ μm
for $I_p > 7.8\ GW/cm^2$ efficiency of conversion 16%
for $I_p = 16\ GW/cm^2$, efficiency 17.6%
surface damage threshold 30 GW/cm^2
vary θ 76-90°, output 5-5.3, 5.9-6.3 μm with quantum efficiency 17%,
output power ~1 MW

R11 - Yu.M. Andreev, V.G. Voevodin, P.P. Geiko, A.I. Gribenyukov, V.V. Zuev, A.S. Solodukhin, S.A. Trushin, V.V. Churakov & S.F. Shubin
Inst.Atmospheric Optics, Tomsk
Transformation of the frequencies of nontraditional (4.3 and 10.4 μm) CO_2 laser radiation bands in $ZnGeP_2$ Sov.J. Quantum Electron. **17** 1362-3 (1987)
Russian Russian ref: Kvantovaia Elektronika **14** 2137-2138 (Nov. 1987)

SHG 4.3 μm + SFG with 10.4 μm
PUMP CHARACTERISTICS:
average power of 4.3μm band did not exceed 10 mW
CRYSTAL: $ZnGeP_2$ Type I interactions 7-13 mm thick
cut at angles $\theta = 53$ & 48.5^o $\varphi = 0$
best results from crystal 7mm length with $\theta = 47^o30'$ and $\varphi = 0$
AR coating gave transmission up to 87.5% @ l = 4.3μ; 73% @ 10.4μ
measured SH phase-matching angle $55^o50'$

R12 - Yu.M. Andreev, V.Yu. Baranov, V.G. Voevodin, P.P. Geiko, A.I. Gribenyukov, S.V. Izyumov, S.M. Kozochin, V.D. Pis'mennyi, Yu.A. Satov & A.P. Strel'tsov
I.V.Kurchatov Institute of Atomic Energy,Moscow
Efficient generation of the second harmonic of a nanosecond CO_2 laser radiation pulse Sov.J.Quantum Electron. **17** 1435-1436 (1987)
Russian Ref.: Kvantovaya Elektronika **14** 2252- 2254 (Nov. 1987)

SHG of CO_2
PUMP CHARACTERISTICS: CO_2 2 ns pulse 9.52 μm
CRYSTAL: type I conversion
second harmonic generator: $\Theta = 76^o$, $\varphi = 0$ length 3 mm
fourth harmonic generator: $\Theta = 47^o$, $\varphi = 0$ length 10 mm both crystals chemodynamic polished, no AR coating
α did not exceed 0.1 cm^{-1} from 2.5-8 μm
calculation showed that that length of 3mm optimal for 1 GW/cm^2
damage threshold for fresh surface 2.5 J/cm^2

R13 - Yu.M. Andreev, P.P. Geiko, V.V. Zuev, V.E. Zuev, O.A. Romanovskii, & S.F. Shubin Inst. Atmospheric Optics, Tomsk
Advances in Gas-Analyzers Based on IR Molecular Lasers
Laser & Optical Remote Sensing: Instrumentation & Techniques, 28 Sept.- 1 Oct. 1987, North Falmouth, MA pp 152-155

SHG & sum frequency addition of CO_2 lines can cover much of the 2-5 and 8-12 μm part of the spectrum

R14 - Yu.M. Andreev, V.G. Voevodin, P.P. Geiko, A.I. Gribenyukov, V.V. Zuev, V.E. Zuev institute of Atmospheric Optics, Tomsk, USSR
Effective source of coherent radiation based on CO_2 lasers and $ZnGeP_2$ frequency converters **Laser & Optical Remote Sensing**: Instrumentation & Techniques, 28 Sept.- 1 Oct. 1987 North Falmouth, MA, Optical Society of America 1987 Technical Digest Series, Vol. 18, pp. 300-303

SHG, FHG, SFG with CO_2 & CO
chart of parameters of frequency converters

	Laser	λ in µm	W/cm2	τ in s
SHG	CO_2	9.23	10^9	$2\ 10^{-9}$
	CO_2	10µm band	10^9	$2\ 10^{-9}$
	SH CO_2	4.64	$0.3\ 10^9$	$2\ 10^{-9}$
	CO_2	9.2....10.8	$6\ 10^7$	$1.7...2\ 10^{-7}$
	CO_2	9.2....10.8	$0.5...1\ 10^6$	$10^{-4}..10^{-2}$
	CO_2	4.3 µm band	-	$1.5....3.3\ 10^{-7}$
	CO_2	9.2....10.8	$2\ 10^5$	CW
	CO	5.3...6.1	-	$4.5\ 10^{-5}$
	CO	5.3...6.1	$2.5\ 10^5$	CW
FHG	CO_2	9.23	$1\ \&\ 0.3\ 10^9$	$2\ 10^{-9}$
	CO_2	9.2....10.6	$6\ 10^7$	$1.7...2\ 10^{-7}$
SFG	CO2	4.3 & 10.4	-	$1.5...3\ 10^{-7}$ & $6\ 10^{-7}$
	CO & CO2	5.3...6.1 & 9.2...10.8	$2\ 10^5$	
	CO:CO2	5.3...6.1 & 9.2...10.6	10^6	$5\ 10^{-5}$

CRYSTAL: boules 20-25 mm diameter X 150 mm length
crystal lengths, 3 mm, 7 - 10.5 mm.

R15. - Yu.M. Andreev, V.G. Voevodin, A.I. Gribenyukov, V.N. Davydov, V.I. Zhuravlev, V.A. Kapitanov, T.D. Lezina, G.A. Struchebrov, and G.S. Khmel'nitskii
Inst. Atmospheric Optics, Tomsk
Beam-path gas analyzer based on a tunable CO_2 laser with frequency doubling
J. Applied Spectroscopy **47**(1) 662-666 (Jan.1988)
Russian ref.: Zhurnal Prikladnoi Spektroskopii **47**(1) 15-20 (July, 1987)

SHG with CO_2
CO_2 LASER: Tuning range 9.2-10.8 µm
Maximum power 50 W
Pulse rep rate up to 1500 Hz
Pulse duration 0.1-10 msec
CRYSTAL: Size 3.6 x 10 X 20 mm
Working temperature of crystal 20-160 °C
Wavelength range of SHG 4.6-5.4 µm

R16 - V.E. Zuev Inst. Atmospheric Optics, Tomsk
Spectroscopic studies of laser sounding of the atmosphere
International Laser Radar Conference, Innichen-San Candido, Italy, 20-24 June 1988
pp.119-121
describes system where ZGP is used as OPO, SHG, & SFG with CO2 & CO pumps
CRYSTAL: sizes up to 20-25 mm diameter & up to 150 mm length

R17 - Yu.M. Andreev, P.P. Geiko, V.V. Zuev, O.A. Romanovskii & S.F. Shubin
Inst. Atmospheric Optics, Tomsk
Control of gas pollution of air medium with the aid of CO_2 and CO lasers equipped with frequency converters
XIII International Conference on Coherent & Nonlinear Optics, Minsk, 6-9 Sept 1988, Part II, Sections IX-XVI, pp. 221-222

SHG & SFG of CO_2
LASER: rep rate 100Hz
pulse length 100 ms
Peak power 150 W
peak power of second harmonic 10 mW

R18 - Yu.M. Andreev, P.P. Geiko & V.V. Zuev
High-efficiency frequency conversion of IR lasers with $ZnGeP_2$ and $CdGeAs_2$
IAO, Tomsk
Advances in Laser Science III. Third International Laser Science Conference Atlantic City,NJ 1-4 Nov. 1987 AIP Conference Proceedings **172** 190-2 (1988), eds. Andrew C. Tam, James L. Gole & William C. Stwalley
Results on $ZnGeP_2$

FC type	Laser	λ in μm	τ in s
SHG	CO2	9.28	2 10-9
	SH CO2	4.64	1.5 10-9
	CO2	9.2-10.8	2 10-7
	CO	5.3-6.1	4 10-5
	CO	4.3	3.3 10-7
FHG	CO2	9.28	2 10-9
SFG	CO2	4.3	3 10-7
		10.4	6 10-7
	CO &	5.3-6.1	CW
	CO2	10.6	CW

CRYSTAL: boules 20-25 mm diameter, up to 150 mm length

R19 - Yu.M. Andreev, P.P. Geiko, V.V. Zuev, O.A. Romanovskii IAO, Tomsk
Gas Analysis Using CO_2 Laser Frequency Converters
Advances in Laser Science III. Third International Laser Science Conference Atlantic City,NJ 1-4 Nov. 1987 AIP Conference Proceedings **172** 193-5 (1988), eds. Andrew C. Tam, James L. Gole & William C. Stwalley

SHG & SFG of CO_2 & CO lasers using ZGP & TAS
frequency doubled 10.3 μm by heating ZGP above 100°C

R20 - V.E. Zuev, M.V. Kabanov, Yu.M. Andreev, V.G. Voevodin, P.P. Geiko, A.I. Gribenyukov, V.V. Zuev Atmospheric Optics Inst., Tomsk
Applications of efficient parametric IR-laser frequency converters
Bull. Academy Sci.,USSR,Physical Sciences **52** 87-92 (1988)
Russian ref.: Izvestiya Akademii Nauk SSSR, Seriya Fizicheskaya **52**(6) 1142-1148 (1988)

plot of efficiency vs. crystal length
CRYSTALS: 20-25 mm diameter X up to 150 mm long
Results for $ZnGeP_2$ crystal

Form	Laser	λ in μm	τ in sec
SHG	CO_2	9.28	$2\ 10^{-9}$
	CO_2	10.2-10.3	
	SH CO_2	4.64	$1.5\ 10^{-9}$
	CO_2	9.2-10.8	$2\ 10^{-7}$
	CO	5.3-6.1	$4\ 10^{-5}$
	CO_2	4.3	$3.3\ 10^{-7}$
FHG	CO_2	9.28	$2\ 10^{-9}$
SFG	CO_2	4.3	$3\ 10^{-9}$
		10.4	$6\ 10^{-7}$
	CO &	4.3	$3\ 10^{-7}$
	CO_2	10.4	$6\ 10^{-7}$

R21 - G.C. Bhar, S. Das, U. Chatterjee, & K.L. Vodopyanov
Burdwan U., India & Gen.Phys. Inst., Moscow
Temperature-tunable second-harmonic generation in zinc germanium diphosphide
Appl.Phys.Lett. **54** 313-314 (1989)

SHG of CO_2
CRYSTAL:

α(3-8μm) less than 0.2 cm^{-1} size 2.5 cm diameter,15 cm length
type I phase match with 48° cut 9.18-9.6μm doubled varying phase match angle and temperature

R22 - Yu.M. Andreev, A.N. Bykanov, A.I. Gribenyukov, V.V. Zuev, V.D. Karyshev, A.V. Kisletsov, I.O. Kovalev, V.I. Konov, G.P. Kuz'min, A.A. Nesterenko, A.E. Osorgin, Yu.M. Starodumov & N.I. Chapliev Inst.General Physics, Moscow
Conversion of pulsed laser radiation from the 9.3-9.6 mm range to the second harmonic in $ZnGeP_2$ crystals
Sov. J. Quantum Electron. **20** 410-414 (1990)
Russian Ref.: Kvantovaya Elektron. **17** 476-480 (April 1990)

SHG of CO_2
PUMP CHARACTERISTICS: pulsed TEA CO_2 tunable 9.2-9.8 μm
110-120 ns spike with 1-1.1 μs low intensity tail
CRYSTAL:

length mm	λ μm	Θ_{pm}	α cm^{-1}
4.6	9.3	64.4	0.8-3.0
4.0	9.3	62.7	0.6-1.2
	9.6	64.9	

1.4x1.4 cm cross section

best Russian crystals had $\alpha(9\mu) = 0.5\text{-}0.4\ cm^{-1}$; $\alpha(4.5\mu) = 0.1\text{-}0.2\ cm^{-1}$
paper includes plots of efficiency vs. a, energy, energy density
also plot of phase matching angle vs. temperature

R23 - K.L. Vodopyanov, L.A. Kulevskii, V.G. Voevodin, A.I. Gribenyukov, K.R. Allakhverdiev, & T.A. Kerimov General Physics Inst., Moscow
High efficiency middle IR parametric superradiance in $ZnGeP_2$ and GaSe crystals pumped by an erbium laser
Optics Communications **83** 322-326 (1991)

OPO
PUMP CHARACTERISTICS:
Er^{3+}:YAG, $\lambda = 2.94\ \mu$ $\tau = 110$ ps ±10, 0.5-2 mJ, rep rate 1.2 Hz
Er^{3+}:YSGG , $\lambda = 2.79\ \mu$

CRYSTALS:	Type I (o-ee)	Type II (o-eo)
Crystal orientation	$\Theta = 47°$, $\varphi = 0$	$\Theta = 84°$, $\varphi = 31°$ (45°optimal)
Range of Θ variation	47-49.55°	76-90°
Tuning range achieved	4-10 μ	5.2-5.6, 6.2-6.7 μ
Crystal length	11 mm	42 mm
Damage threshold	6.5 GW/cm^2	30 GW/cm^2

R24 - Yu.M. Andreev, P.P. Geiko & G.M. Krekov Tomsk Medicine Institute, Tomsk
O.A. Romanovskii Inst. Atmosheric Optics, Tomsk
Detection of trace concentration of some simple pollutants in Tomsk
SPIE Vol. **1811** High-Resolution Molecular Spectroscopy pp. 367-370 (1991)

SHG, SFG of CO_2 also THG using TAS

R25 - K.L. Vodopyanov, L.A. Kulevskii, A.I. Gribenyukov, and K.R. Allakhverdiev
General Physics Inst., Moscow
High efficiency middle IR parametric superradiance in $ZnGeP_2$ and GaSe crystals pumped by an erbium laser
Journal de Physique IV: Colloque 7, supplement au Journal de Physique III, Vol. 1, Decembre 1991 pp. C7-391 - C7-394
same as R23?

R26 - A.A. Betin, V.G. Voevodin, K.V. Ergakov, A.V. Kirsanov & V.P. Novikov
Inst. Applied Physics, Siberian Polytechnical Inst.,Tomsk
Generator of infrared radiation at the second-harmonic frequency of a TEA CO_2 laser
Sov.J. Quantum Electron. **21** 735-738 (1991)
Russian Ref.: Kvantovaya Elektron. **18** 812-816 (July 1991)

SHG of CO_2
PUMP CHARACTERISTICS: TEA CO_2 short peak 170-200 ns + μs tail
maximum energy per pulse 3J
CRYSTAL: $\alpha(CO_2) = 0.3\text{-}2\ cm^{-1}$

max breakdown threshold after mechanical polish + surface treatment 60-80 MW/cm^2(10-15 J/cm^2);
after chemodynamic polish 40-60 MW/cm^2
absorption band in 9.0-9.1 μm range :
max. absorption in best crystals 0.3 cm^{-1}; worst, 1.5 cm^{-1}
best large crystals, ~ 1 cm , a(3-8μm) not more than 0.1 cm^{-1}
α(TEA CO_2 fundamental) = 0.35- 0.70 cm^{-1}
room temperature phase matching ends at 10.2 μm
max. in SHG energy observed for λ = 10.55 μm at T=160-190°C with
$\Theta_{pm} = 76°$; crystals degrade above 400° C
talk about greater than 5 cm crystals;
9.3mm & 9.8mm long with 2 cm^2 aperture
damage threshold 45 MW/cm^2
noted considerable absorption inhomogeneity over face, up to a factor of 3 or 4
obtained an external efficiency of 6-8% (surfaces not AR coated)
maximum energy of SH pulse was 0.16 J

R27 - J.H. Churnside, J.J. Wilson, A.I. Gribenyukov, S.F. Shubin, S.I. Dolgii, Y.M. Andreev, V.V. Zuev Wave Propagation Lab., Boulder & Institute for Atmospheric Optics, Tomsk
Frequency conversion of a CO_2 Laser with $ZnGeP_2$
NOAA Technical Memorandum ERL WPL-224 July, 1992

SHG & FHG of CO_2
SHG conversion efficiency 26%
FHG (2 SHG) conversion efficiency 0.04%

R28 - Yu.M. Andreev, S.D. Velikanov, A.S. Yerutin, A.F. Zapol'skii, D.V. Konkin, S.N. Mishkin, S.V. Smirnov, Yu.N. Frolov, and V.V. Shchurov
All-Russian Scientific-Research Institute of Experimental Physics, Arzamas-16, Nizhnii Novgorod Oblast
Second Harmonic generation from DF laser radiation in $ZnGeP_2$
Sov. J. Quantum Electronics **22**(11) 1035 (November 1992)
Russian ref.: Kvantovaya Elektron.(Moscow) **19** 1110 (November 1992)

SHG of DF
pulse length sharp rise with trailing edge: 150 ns(half.max),500 ns (at 0.1)
crystal length 10.1 mm, external efficiency 4%:internal eff. 7.6%
" " 13.6 " " 6.2%; " " 11.8%

R29 - K.L. Vodopyanov General Physics Inst., Moscow
Parametric generation of tunable infrared radiation in $ZnGeP_2$ and GaSe pumped at 3 μm J.Opt.Soc.Am.B **10**(9) 1723-1729 (September 1993)

OPO pumped by Er^{3+}:YAG (2.94μm) or Er^{3+}:Cr^{3+}:YSGG(2.79 μm)

Property	Type I (o-ee)	Type II (o-eo)
Crystal orientation	$\theta = 47^0$, $\varphi = 0^0$	$\theta = 84^0$, $\varphi = 31^0$
Range of q variation	47-49.55 deg	76-90 deg
Tuning range on μm	4-10	5.2-5.6, 6.2-6.7
Crystal length in mm	12	42
Walk-off in mm	0.14(θ=48^0)	0.11(θ=84^0)
Effective length	12	19
OPG threshold GW/cm^2	0.5	0.35
I_{max} used "	6.5	30
Max. OPG quantum eff.	3%	17.6%
I_{damage} GW/cm^2	6.5	30

R30- A.A. Barykin, S.V. Davydov, V.D. Dorokhov, V.P. Zakharov, & V.V. Butuzov
Samarskoe Science-Industrial Union for Automated Systems
Generation of the second harmonic of CO_2 laser pulses in a $ZnGeP_2$ crystal
Quantum Electronics **23**(8) 688-693 (August 1993)
Russian ref.: Kvantovaya Elektron. **20** 794-800 (August 1993)

SHG of CO_2
CRYSTAL: 12.5 X 10.62 x 7.2 mm length
9.3-9.6 μm to 4.6-4.8 μm

R31 - K.L. Vodop'yanov General Physics Inst., Moscow
Yu.A. Andreev Siberian State Medical University, Tomsk
G.C. Bhar Burdwan Univ., Burdwan, India
Parametric superluminescence in a $ZnGeP_2$ crystal with temperature tuning and pumping by an erbium laser Quantum Electronics **23**(9) 763-766 (Sept. 1993)
Russian ref.: Kvantovaya Elektron. **20** 879-882 (September 1993)

OPO
PUMP: Q-switched Er:YSGG laser, l = 2.79 μm, repition rate 1.2 Hz
working energy reached 20 J
single pulse from resonator, 100 ps, energy 0.5-1 mJ
CRYSTAL: length 42 mm in direction of Type II phase matching
$\theta = 84^o$ and $\varphi = 31^o$
by temperature tuning could reach 5.3 - 5.9 μm
threshold energy density for superluminescence 0.35 GW/cm^2
working pump energy density 5-10 GW/cm^2 at superluminescence efficiency of 10% and damage threshold of 35 GW/cm^2

R32 - K.L. Vodopyanov General Physics Inst., Moscow
Imperial College, London

2.8 μm Er-laser pumped nonlinear devices
pp.10-13 in **Technical Digest: EQEC'93-EQUAP'93**,Vol.I, Frienze, Italy, 10-13 September 1993, edited by P. de Natale, R. Meucci, S. Pelli

OPO
PUMP: flashlamp pumped Er^{3+}:Cr^{3+}:YSGG @ $\lambda = 2.8\mu m$
Q-switched, single pulses 100 ± 10 ps TEM_{00} mode, 0.5 mJ
after amplification, 2-4 mJ
repetition rate 1-3 sec
when a passive InAs shutter was added, got 30-50 ps pulses
CRYSTAL: length 12 mm for angle tuning
for Type II interaction, length = 42 mm
OPO Type I tuning range 4-10 μm
Type II tuning range 5-6.3 μm, quantum efficiency 18%
Travelling wave OPO threshold 0.35 GW/cm^2, which is 100 times smaller than the optical damage threshold

R33 - K.L. Vodopyanov General Physics Inst., Moscow
Imperial College, London

2.8 μm Er-laser-pumped non-linear devices
Leituvos fizikos zurnalas **33** (5-6) 301-304 (1993)
OPO
PUMP: mode-locked Sr:Cr:YSGG laser @ $\lambda = 2.8\mu m$
single pulses 100 ± 10 ps, TEM_{00} mode, about 0.5 mJ
CRYSTALS: L = 11 mm, $\theta = 47^o$ for Type I phase matching and
L = 42 mm, $\theta = 84^o$ for Type II phase matching
OPO Type II tuning covered 5-5.3 μm (signal) and 5.9-6.3 μm (idler)
with typical linewidth of 10-20 cm^{-1}
OPG threshold was as low as 0.35 GW/cm^2
surface damage threshold for 100 ps 2.8 μm pulses was 30 GW/cm^2
Type I had broad OPG lines especially near degeneracy, 1300 cm^{-1}
at $\lambda = 10$ μm got linewidth of 50 cm^{-1}
4-10 μm tuning was achieved with 1-2% efficiency
OPG threshold as low as 0.25 GW/cm^2 for 2.8 μm pump

R34 - Konstantin L. Vodopyanov General Physics Inst., Moscow
Imperial College, London

Wide tuning range OPG's pumped by short Er-laser pulses at $\lambda = 2.8$ μm
Advanced Solid State Lasers, OSA Proceedings, Vol. **24**, Memphis, TN 30 Jan-2 Feb 1995, 194-197, [1995 Technical Digest, Vol. 8,pp.340-342,WG3-1-3]

PUMP: $Er^{3+}:Cr^{3+}$:YSGG laser, $\lambda = 2.8\ \mu m$, rep rate 3 Hz
with active mode locking, $\tau = 90$ ps, with 0.7 mJ
with passive mode locking, 30-50 ps pulses,
after amplification 3-4 mJ energy per pulse
Travelling-wave Optical Parametric Generator(TOPG):
ZGP tuning range, 3.9-10 μm, for both type I & II
OPG pump threshold, 0.25 GW/cm^2 for 11 mm long crystal
Type II had conversion efficiency up to 18% for MW peak power
with linewidth 30-40 cm-1
Type I broader linewidth especially near degeneracy point

R35 - K.L. Vodopyanov Imperial College, London
V.G. Voevodin Siberian Physical-Technical Inst.,Tomsk
Type I and II ZnGeP2 travelling-wave optical parametric generator tunable between 3.9 and 10 μm
Optics Communications **117** 277-282 (1995)

PUMP: mode locked $Er^{3+}:Cr^{3+}$:YSGG laser @ $\lambda = 2.8\mu m$
pulse duration 100 ± 10 ps, energy 2-3 mJ, rep rate 3 Hz
CRYSTAL: Type I ($o \rightarrow ee$): L= 11 mm, $\theta = 47^o$ -cut, $\varphi = 0^o$ (walk-off 0.13 mm)
Type II($o \rightarrow eo$): L = 30 & 17 mm, $\theta = 63.5^o$, $\varphi = 31o$
(walk-off 0.3 & 0.17 mm)
OPG: Type I tuning range_ 3.9 - 10 μm
Type II tuning ranges_ signal 6 - 10 μm, idler 3.9 - 5.1 μm
OPG linewidths exp. & theor. given at various wavelengths
OPG thresholds for 2.8 μm pump for various lengths given

R36 - Yu.M. Andreev, V.V. Butuzov, G.A. Verozub, A.I. Gribenyukov,
S.V. Davydov, and V.P. Zakharov Samara State Research & Production Association of Automatic Systems, Samara, Russia
Generation of the second harmonic of pulsed CO_2-laser radiation in $AgGaSe_2$ and $ZnGeP_2$ single crystals
Laser Physics **5**(5) 1014-1019 (1995)
SHG
PUMP CHARACTERISTICS:
pulsed electric discharge CO_2 laser
output radiation energy 150 mJ
output aperture 6.8 mm
FWHM of leading spike $\tau_1 \equiv \tau_{0.5} \sim 45$ -50 ns
with total pulse duration about 100 ns
maximum gain lines at $\lambda = 9.3, 9.59, 10.26, 10.61\ \mu m$

PUMP: Er^{3+}:Cr^{3+}:YSGG laser, $\lambda = 2.8\ \mu m$, rep rate 3 Hz
with active mode locking, $\tau = 90$ ps, with 0.7 mJ
with passive mode locking, 30-50 ps pulses,
after amplification 3-4 mJ energy per pulse
Travelling-wave Optical Parametric Generator(TOPG):
ZGP tuning range, 3.9-10 μm, for both type I & II
OPG pump threshold, 0.25 GW/cm^2 for 11 mm long crystal
Type II had conversion efficiency up to 18% for MW peak power
with linewidth 30-40 cm-1
Type I broader linewidth especially near degeneracy point

R35 - K.L. Vodopyanov Imperial College, London
V.G. Voevodin Siberian Physical-Technical Inst.,Tomsk
Type I and II ZnGeP2 travelling-wave optical parametric generator tunable between 3.9 and 10 μm
Optics Communications **117** 277-282 (1995)

PUMP: mode locked Er^{3+}:Cr^{3+}:YSGG laser @ $\lambda = 2.8\mu m$
pulse duration 100 $\pm$ 10 ps, energy 2-3 mJ, rep rate 3 Hz
CRYSTAL: Type I (o$\rightarrow$ee): L= 11 mm, $\theta = 47^o$ -cut, $\varphi = 0^o$ (walk-off 0.13 mm)
Type II(o$\rightarrow$eo): L = 30 & 17 mm, $\theta = 63.5^o$, φ = 31o
(walk-off 0.3 & 0.17 mm)
OPG: Type I tuning range_ 3.9 - 10 μm
Type II tuning ranges_ signal 6 - 10 μm, idler 3.9 - 5.1 μm
OPG linewidths exp. & theor. given at various wavelengths
OPG thresholds for 2.8 μm pump for various lengths given

R36 - Yu.M. Andreev, V.V. Butuzov, G.A. Verozub, A.I. Gribenyukov,
S.V. Davydov, and V.P. Zakharov Samara State Research & Production Association of Automatic Systems, Samara, Russia
Generation of the second harmonic of pulsed CO_2-laser radiation in $AgGaSe_2$ and $ZnGeP_2$ single crystals
Laser Physics **5**(5) 1014-1019 (1995)
SHG
PUMP CHARACTERISTICS:
pulsed electric discharge CO_2 laser
output radiation energy 150 mJ
output aperture 6.8 mm
FWHM of leading spike $\tau_1 \int \tau_{0.5} \sim 45$ -50 ns
with total pulse duration about 100 ns
maximum gain lines at λ = 9.3, 9.59, 10.26, 10.61 μm

CRYSTALS:

No.	Thickness in mm	Area of face in mm^2	Angle of shear plane of Xtal	Absorption Coefficient at λ_1	λ_2 in cm^{-1}
1	12	10 x 15	75 deg	0.7	0.01
2	7.2	12.5 x 10.62	76	0.8	0.4
3	10.4	7.3 x 15	72	0.7	0.01

R37 - Konstantin L. Vodopyanov and Chris C. Phillips
Imperial College, London

Travelling wave mid-IR ZnGeP2 and GaSe optical parametric generators and their spectroscopic applications, pp.170-174 in **Solid State Lasers and Nonlinear Crystals**, 5-7 February 1995, San Jose, CA, edited by Gregory J. Quarles, Leon Esterowitz and L.K. Cheng, SPIE Proceedings Vol. 2379

OPO

PUMP CHARACTERISTICS: Er^{3+}:Cr^{3+}: YSGG laser @ $\lambda = 2.79\ \mu m$

pulse length $\tau = 100 \pm 10$ ps, TEM_{OO}, rep rate 3 Hz

energy about 0.5 mJ, after passing through amplifier 2-4 mJ

CRYSTAL: absorption at pump wavelength, $\alpha < 0.1\ cm^{-1}$

lengths: Type I, 11 mm; Type II. 42 and 30 m

tuning range 4-10 µm for both I & II

typical quantum efficiency 1-2 %; for type II, near degeneracy, achieved 18%

QPG threshold intensity was 0.24-0.35 GW/cm^2, a value 100 times smaller than the optical damage threshold

SUMMARY OF RUSSIAN $ZnGeP_2$ NLO WORK

SUM FREQUENCY GENERATOR (SFG)

Nd:YAG + CO_2	1
$CO + CO_2$	7,14,16,18, 20
4.3 + 10.4 μm	11,14
$CO_2 + CO_2$	13,17, 18, 19, 20, 21, 24

SECOND HARMONIC GENERATOR (SHG)

CO_2	2,6,9,12,13,14,16,17,18,19,20,21, 22,24,26,27,30,36
CO	3,8,17
4.3 μm	11
DF	28

FOURTH HARMONIC GENERATOR (FHG)

CO_2	3,14,15,18,20,27

OPTICAL PARAMETRIC OSCILLATOR (OPO)

Er:YALO	4,5
Er:Cr:YSGG	11,23,25,29,31,32,33,34,35, 37
Er:YAG	23,25,29

RECENT WESTERN WORK IN $ZnGeP_2$

C1 - P.A. Budni, K. Ezzo, P.G. Schunemann, S. Minnigh, J.C. McCarthy & T.M. Pollak, "2.8 micron pumped optical parametric oscillation in $ZnGeP_2$", pp.334-338 in **Advanced Solid State Lasers,** Hilton Head, South Carolina, 18-20 March **1991**, editors George Dube and Lloyd Chase, Optical Society of America Proceedings, Vol. 10

PUMP: methane Raman shifted Nd:YAG 1.06μm ⇒ 2.8 μm
max SRS output 2.1 mj

CRYSTAL: 6x6x18 mm, faces cut normal to ⟨102⟩ direction
$\alpha(2.8\mu m) = 0.06\ cm^{-1}$, $\alpha(5.6\mu m) < 0.02\ cm^{-1}$

OPO RESULTS: Type I phase matching. For Input, 2.1 mj, spot size 1.2 mm, 8-12 ns pulsewidth get peak power density up to 45 MW/cm^2, 150 μj per pulse, for an optical efficiency of 7%
Threshold for OPO output, 18-20 MW/cm^2

C2 - Norman P. Barnes, "Tunable mid-infrared sources using second-order nonlinearities", International Journal of Nonlinear Optical Physics, **1**, 639-672 (1991)

internal phase-matching angles vs wavelength for 1.73 & 2.10 μm pumps, range of incident angles 63^o for 1.73μm; 13^o for 2.10μm

C3 - P.A. Budni. P.G. Schunemann, M.G. Knights, T.M. Pollak & E.P. Chicklis, "Efficient, high average power optical parametric oscillator using $ZnGeP_2$", pp. 380-383 in **Advanced Solid State Lasers,** Sante Fe, New Mexico, 17-19 February **1992**, editors Lloyd L. Chase & Albert A. Pinto, OSA Proceedings, Vol. 13

PUMP: 2μm from diode pumped, repetitively Q-switched Tm,Ho:YLF oscillator amplified by tungsten-lamp pumped Er,Tm,Ho:YLF amplifier. At 77K, 40 W average power output, pulse repetition frequency (PRF) 1-90 kHz, FWHM pulsewidth 15-525 ns. A 2-pass pre-amplifier output is 10 W: with 2 single pass stages added, the total power output > 40 W

CRYSTAL: 6x6x12 mm, boule grown along [112], $\alpha(2.05\mu m)=0.26\ cm^{-1}$
Type I phase matching, $\theta = 55^o$.

OPO RESULTS: Using 10 W input: rep rate 2.5 kHz, 23 ns pulsewidth, 28.5% slope efficiency ; 4 kHz, 27 ns, 27.3%, highest overall efficiency, 18%; using 13 W input: 10 kHz, 28 ns, highest total power, 1.6 W
Continuous tunability from 3.45 - 5.05 μm.

C4 - M. Knights & P. Budni, **Tunable Mid-IR Laser Program** , Final Technical Report, WL-TR-92-5031, August 1992, Wright Laboratory, Solid State Electronics Directorate, WL/ELOS, Contract F33615-89-C-1059

OPO

PUMP: 2 μm holmium YLF laser and amplifier, TEM_{00} output average power of 44 Watts with pulsewidths of 25 ns @ 10 kHz
Pump repetition rates of 2.5, 4, 10, 20 and 30 kHz had pump pulsewidths of 23, 27, 28, 60 and 97 nsecs respectively

CRYSTAL: type I phase matching, $\theta = 55^o$, 6 x 6 x 12 mm
experimentally verified 2 μm pumped phase matching curve over 3.45-5.05 μm range energy slope conversion efficiency of 28.5% and overall conversion to 18% achieved @ 2.5 kHz; conversion efficiency of 27.3 % @ 4 kHz demonstrated high PRF operation: 2-30 kHz demonstrated 1.6 W average power @ 10 kHz for 13 W input: 1.4 W @ 20 kHz; 0.8 W @ 30 kHz

C5 - M. Knights & P. Budni, **Characterization of $AgGaSe_2$ and $ZnGeP_2$ OPO's Pumped with High Power 2 Micron Lasers,** Final Technical Report, WL-TR-93-5016, November 1992, Wright Laboratory, Solid State Electronics Directorate, WL/ELOS, Contract F33615-89-C-1059, modification P0007

OPO

PUMP: Cryogenically cooled, diode pumped Ho:YLF @ 2μm
3W CW or Q-switched @ 1.5 kHz with 18-nsec FWHM
high power thermal effects used 20 W CW multimode tungsten pumped LN_2 oscillator

OPO RESULTS: absorption coefficient α_o is temperature dependent.

$\alpha_o(300^oK) = 2 \times \alpha_o(77^oK)$

α_e shows no change with temperature
beam diameter 0.57 mm $1/e^2$ points

For high loss ZGP crystals ($\alpha_o = 0.36 cm^{-1}$),length 14.5 mm long
slope effociency is 6% @300^oK and 27% @ 77^oK
with α_o = 0.26 cm-1 crystal, slope efficiency is 37.5%

C6 - P.G. Schunemann, P.A. Budni, M.G. Knights, T.M. Pollak, E.P. Chicklis, & C.L. Marquardt, "Recent advances in $ZnGeP_2$ mid-IR optical parametric oscillators", 131-133, **Advanced Solid-State Lasers / Compact Blue-Green Lasers**, New Orleans, Louisiana, 1-4 February **1993**, Optical Society of America 1993 Technical Digest Series Vol.2; pp. 166-168 in **OSA Proceedings on Advanced Solid-State Lasers, Vol 15**, A.A. Pinto and T.Y. Fan, ed., (Optical Society of America, Washington, DC 1993)

OPO

PUMP LASER: diode pumped A/O Q-switched Tm:Ho:YLF @ 77 K
λ = 2.05 μm, TEM_{00} mode, linearly polarized,
pulse width 18 ±1 nsec (FWHM)
rep rate 1500 Hz, $1/e^2$ diameter = 0.57 mm at center of Xtal

CRYSTALS: 6x6x11 mm^3 & 4.5X4.5x14.6 mm^3

Orientation $\Theta = 55^o$ for Type I phasematch @ 2.05 μm pump

Absorption coefficients @ 2.05 μm : (α_o=0.26; α_e=0.58) cm^{-1} &

(α_o=0.38; α_e=0.77) cm^{-1} respectively @ RT

In situ: high loss crystal @ 2.05 μm measured

α_o=0.36±0.01 cm^{-1}; α_e = 0.78±0.01 cm^{-1} @ RT;

α_o=0.17±0.01 cm^{-1}; α_e = 0.77±0.01 cm^{-1} @ LNT

AR Coatings: each 2.05 μm & 3.5-5.0 μm

Laser damage theshold: > 1.2 J/cm^2

OPO RESULTS: Collinearly pumped & doubly resonant

Low loss Xtal @ RT: total power conversion efficiency = 26%
with 679 mW threshold, 37% slope
maximum sustained power output: 585 mW @ pump
fluence ≈ 1.2 J/.cm^2

High loss Xtal : @ RT, threshold was 520 mW and slope ≈ 6%
@LNT, threshold ≈ 400 mW and slope efficiency ≈ 25% after
realignment at LNT, threshold was 295 mW and slope efficiency
was 27%. Pumping with 2.3 W obtained OPO output of 552 mW,
an absolute power conversion efficiency of 24%

C7 - M.G. Knights, P.A. Budni, P.G. Schunemann, T.M. Pollak, & E.P. Chicklis,"Multi-watt mid-IR optical parametric oscillator using $ZnGeP_2$", 259-261, OSA Topical Meeting on **Advanced Solid State Lasers,** Salt Lake City, UT, 7-10 Feb **1994**, OSA 1994 Technical Digest Vol.20

OPO

PUMP LASER: Q-switched Tm,Ho:YLF @2.06μm + single-pass rod amplifier capable of 9 W, 6.5 W incident on OPO corresponding to 1.6 mJ/pulse @ 4 KHz. Focussed to beam waist of 600 μm, this yielded 1.15 J/cm^2 or 144 MW/cm^2 in 8 nsec.

CRYSTAL: 6x6x11 mm, $\Theta = 55^o$, α_o(2.05μm) = 0.26 cm^{-1}

OPO RESULTS: Doubly resonant oscillator with double degenercy point at 4.1 μm.

Highest average power achieved was 2.66 W with conversion efficiency of 40%. [3.3 W output shown at meeting].
Highest conversion efficiency was 46% @ 4.65 W drive level.
First 4 data points yield a slope efficiency of ≈ 65% which extrapolates to a threshold of 1.32 W pump input.

C8 - C.L. Marquardt, W.T. Whitney, B.J. Feldman, G.C. Catella, D.S. Burlage, M.G. Knights, P.A. Budni, & P.G. Schunemann, "Thermal effects in zinc germanium phosphide optical parametric oscillators", 201, **CLEO'94, Summaries of papers presented ay the Conference on Lasers and Electro-Optics,** Anaheim, CA, 8-13 May 1994, Optical Society of America 1994 Technical Digest Series Vol. 8

C9 - P.D. Mason, D.J. Jackson & E.K. Gorton
CO_2 laser frequency doubling in $ZnGeP_2$
Optics Comm. **110** 163-166 (1994)
Erratum Optics Comm. **114** 529 (1995)
SHG
PUMP: TEA CO_2 laser. single axial mode, 9P(20) transition, $\lambda = 9.55\ \mu m$.
Typical peak power 14 kW, pulse duration 240 ns (FWHM)
CRYSTAL: 7.7x7.5 mm aperture, 1 cm long, cut 70° to c-axis
$\alpha(9.6\ \mu m) = 0.56\ cm^{-1}$, $\alpha(4.8\ \mu m) = 0.155\ cm^{-1}$
RESULTS: For 9.55 μm, phase match angle 67.7°
Maximum peak conversion efficiency was 8.1% for a pump internal intensity of 30 MW/cm^2 and energy density 18 J/cm^2

C10 - Norman P. Barnes, Keith E. Murray, Mehendra G. Jani, & Thomas M. Pollak, WG5-1-3, 346-349,"$ZnGeP_2$ parametric amplifier", **Technical Digest- Advanced Solid State Lasers**, Memphis TN, 30 Jan- 2 Feb 1995, Optical Society of America
OPA
PUMP: Ho:Tm:Er:YLF @ 2.06 μm, pulse length ≈50 ns, 30 mJ
CRYSTAL: 9 mm long
SIGNAL: 3.39 μm from HeNe was absorbed in ZGP yielding gain of ≈0.7 single pass, small signal gain was 10 for 2.064 μm

C11 - J.M Auerhammer, A.F.G. van der Meer, & P. W. van Amersfoort, "Effecient frequency doubling of picosecond pulses of a free-electron laser in $ZnGeP_2$", Paper CTuI20, CLEO/QELS 95, Baltimore, MD, 23 May 1995, CLEO'95, Vol. 15,1995 Technical Digest Series OSA, P.99, (p.87 Advance Program)
SHG
PUMP: free-electron laser,FELIX, $\lambda = 5.5\text{-}9.0\ \mu m$, high-power, short-pulse external efficiencies 49% - 15%
At $\lambda = 7.8\ \mu m$, generated 14 mW of SHG average power, 0.8 MW peak power, pulse energy 0.8μJ.
CRYSTAL: 7 mm long, Type I phase matching

C12 - J.M. Auerhammer, A.F.G. van-der-Meer, P.W. van-Amersfoort, Q.H.F. Vrehen & E.R. Eliel, "Effecient frequency doubling of ps-pulses from a free-electron laser in $ZnGeP_2$", Optics Communications, **118** 85-89 (1995)

PUMP: FELIX (free electron laser for infrared experiments), p-polarized, 5-110 μm, 1 ps pulses at 1 GHz rep rate contained inside 'macropulse' typically 5 μs repeated every 200 ms. Average power of laser 10-100 mW. Experiments done at $\lambda = 5.5, 6.3, 7.8, 8.3\ \&\ 9.0\ \mu m$. Measured external conversion efficiences η_{ext} are respectively: 0.48, 0.46. 0.36, 0.29 & 0.12,for 1 MW incident power.
CRYSTAL: 7 mm long, Type I phase matching

APPENDIX

The following pages are a bibliography of nonlinear optics use of $ZnGeP_2$, listed alphabetically by first author.

ZnGeP2

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